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(54) Title: **MOLDABLE MATRIX POLYMER MATERIAL, MOLDED COMPOSITE PRODUCT AND METHOD FOR MAKING SAME**

(57) Abstract: A moldable matrix polymer material is disclosed which is useful for making reinforcing articles for use in the manufacture of molded composite articles. The moldable matrix polymer material comprises a moldable matrix polymer resin and a catalyst composition. The invention is also directed to a molded composite product made from the moldable matrix polymer material and a string binder.

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MOLDABLE MATRIX POLYMER MATERIAL,
MOLDED COMPOSITE PRODUCT AND METHOD FOR MAKING SAME

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5 APPLICABILITY OF THE INVENTION

 The invention relates to a moldable matrix polymer material, a molded composite product made there from, and to methods for preparing the same. While the invention is subject to a wide range of applications, the molded products of the present invention are especially suited for use as reinforced composite applications, and will be particularly
10 described in that connection. For example, the molded products of the present invention may be used by the automobile industry as automobile parts, for example, truck beds.

BACKGROUND OF THE INVENTION

 Reinforcing fiber materials comprising glass, polymer, other reinforcing fibers, or
15 blends thereof are commonly used as reinforcement materials in molded composites. These reinforcing fiber materials, when incorporated into the matrix resin of such molded composites, provide the finished product with a higher level of tensile strength and durability than could be achieved if either the reinforcing fibers or the matrix resins were used separately. Reinforcing fibers may be incorporated into a composite matrix resin
20 either in continuous form, as is done in the manufacture of filament-wound composites, or, alternatively, the reinforcing fibers may be introduced into the composite matrix resin as chopped segments that may be dispersed throughout the composite matrix in linear or random fashion, depending on the characteristics that are desired in the final molded composite product.

25 Generally, in the manufacture of reinforcement materials such as preforms that are used in liquid resin molding processes, chopped segments of a reinforcing fiber material, which is also referred to herein as a "fibrous carrier substrate", are combined with a binder resin, after which the resulting composition is laid down over a porous form and solidified. The resulting solidified, matted structure is known as a preform. The fibrous
30 carrier substrate is typically of glass, and may, for example, be a glass strand. The preform made from the combination of the binder resin and the glass carrier substrate can then be cured and/or subjected to a liquid resin molding processes to form the molded composite end product.

Several means of combining the binder resin with the glass carrier substrate to make preforms are known in the art. These means include using emulsified binder resin compositions, dry binder resin compositions or molten binder resin compositions in combination with the glass carrier substrate. For example, an emulsion binder
5 composition comprising a heat-curable binder resin in a diluent or solvent may be blended with the glass carrier substrate; or the binder resin and the glass carrier substrate may be combined in a diluent to form a slurry. Either the emulsion or the slurry may then be poured onto a porous form or mold and suction or a vacuum applied to remove the diluent or solvent component, thereby solidifying the preform. The drawbacks associated with
10 using an emulsion binder include the requirement for extensive clean-up of the forming screens; environmental hazards relating to the discharge of solvent or diluent vapors containing volatile organic chemicals (VOCs); risks to the safety of personnel from exposure to such chemicals; and added costs arising from a lengthy drying period or the need for additional equipment to prepare the preform.

15 Dry binder resin compositions comprising, for example, a powdered binder resin, are also known for use in making preforms. See, for example, U.S. Patent No. 6,054,177. The powdered binder resin is heated sufficiently to melt and cure the binder resin after it is combined with the carrier material. One disadvantage of using the powdered binder resin is that it may be difficult to control the amount of binder powder required to create
20 an acceptable preform. Excess powdered binder resin, when melted, results in the presence of excess molten resin, which may foul equipment and require extensive cleanup operations.

Alternatively, a molten binder resin that is obtained from a source other than a powdered binder resin may be combined with the fibrous carrier substrate to make a
25 preform. To make such a preform using molten binder, typically strands of glass carrier substrate are chopped into segments, which are combined with the binder resin and placed over a porous structural form such as a mesh screen. Alternatively, the strands of glass carrier substrate material are chopped into segments and sprayed over the porous structural form, after which a binder resin is added. The method of adding the binder
30 resin may be via a flame-spray process, in which solid, powdered binder resin is sprayed through a flame immediately before it contacts the glass carrier substrate. In this fashion, the binder resin is melted before it mixes with the glass carrier substrate. A process involving the steps of heating, curing and cooling of the material is then applied to form,

shape and consolidate the mixture, as well as to remove any solvents or diluents that may be present. In this manner, the product is solidified into a preform ready for molding or further processing. The solidified preform may then be removed and used in a subsequent molding operation, such as injection molding, in which a molding resin is injected around
5 the preform and the combination is then cured to form a structurally molded composite.

Because this technique of making the preform typically requires applying an excess of binder resin that eventually melts during the manufacturing process, a commonly observed drawback is the build-up of excess molten binder resin on the equipment, the removal of which is both costly and time-consuming. Moreover, the
10 process includes the inherent difficulties of dealing with the molten binder resin. For example, the process of adding the binder resin is difficult to control, and the handling of the hot, molten binder resin poses an additional safety concern.

Continuous glass fiber strands that have been pre-impregnated with a binder resin may also be chopped into fiber strand segments for preform manufacture. The pre-
15 impregnated strands, known as string binders, may be formed by applying one or more layers of a binder resin onto the surface of a continuous glass fiber strand after it is formed, then allowing the binder resin to solidify on the surface of the strand. After the coating of binder resin is solidified, the coated strand is then chopped into string binder segments that may be used in a spray-up process to make preforms.

20 However, when such string binders and preforms are used to prepare molded products, there is a possibility that insufficient cure occurs when the preform is heated during the molding process, causing uncured binder to migrate to the surface of the molded product. This is commonly referred to as "bleeding." This migration of uncured binder to the surface of the molded product can cause various problems, for example,
25 insufficient bonding between the molded product and any subsequent layers of paint that may be applied, which in turn can cause the paint to blister and peel.

There is, therefore, a need for a molded composite product made from string binders and preforms wherein the extent of cure and cure rates of the binder resin used therein are improved. There is also a need for a moldable matrix polymer material for use
30 in the manufacture of such molded composite products that aids the extent of cure of the binder resins used therein. Further, there exists a need for a method of preparing such molded products having an improved extent of cure and cure rates of the binder resin used therein. These needs are met by the invention described herein.

SUMMARY OF THE INVENTION

Accordingly, the present invention is directed to a moldable matrix polymer material, a molded composite product and a method for making the same, which
5 substantially obviates one or more of the problems due to limitations and disadvantages of the related art.

Additional features and advantages of the invention will be set forth in the description which follows, and in part will be apparent from the description, or may be learned by practice of the invention. The objectives and other advantages of the invention
10 will be realized and attained by the products and methods particularly pointed out in the written description and claims.

To achieve these and other advantages and in accordance with the purpose of the invention, as embodied and broadly described, the invention includes a moldable matrix polymer material useful for preparing molded composite products comprising a moldable
15 matrix polymer resin and a catalyst.

In another aspect, the present invention includes a molded composite product prepared from a string binder, and a moldable matrix polymer material, wherein the moldable matrix polymer comprises a catalyst.

In another aspect, the invention includes a method for making a molded composite
20 product comprising the steps of:

- (a) forming a string binder;
- (b) introducing a moldable matrix polymer material around the string binder, wherein the moldable matrix polymer material comprises a moldable matrix polymer resin and a catalyst composition; and
25
- (c) curing the moldable matrix polymer to form the molded composite product.

It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory, and are intended to provide further explanation of the invention as claimed.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

The moldable matrix polymer material of the present invention comprises a
5 moldable matrix polymer resin and a catalyst composition. The moldable matrix polymer
material is particularly useful for use in the manufacture of molded composite products of
the present invention that are preferably made from string binders or from preforms made
from string binders. Although any suitable string binders and preforms may be used with
the moldable matrix polymer material of the present invention, preferred string binders
10 and preforms are described below.

Any suitable moldable matrix polymer resin that is compatible with the thermoset
binder resin material of the string binder that may be used in the preform can be used.
Suitable moldable matrix polymer resins include vinyl esters, polyesters, urethanes,
epoxies and phenolic thermoplastics. Preferably, the moldable matrix polymer resin is a
15 polyurethane or polyester polymer that is compatible with the low-acid binder resin
material that is preferably present in the preferred string binders. More preferably, the
moldable matrix polymer resin is a polyurethane. The polyurethane polymer may be
added to the string binder or preform directly, or the polyurethane polymer may be formed
in situ around the string binder or preform. For example, a polyisocyanate and a suitable
20 hydroxyl-containing material may be injected around a preform and simultaneously
reacted to form a polyurethane. Preferably, the hydroxyl-containing material is a polyol.
In a preferred embodiment, the polyisocyanate is polymeric MDI, Baydur 425 IMR
polyisocyanate, commercially available from Bayer Corporation (Polymers Division) and
the polyol is Baydur 425 IMR polyol, commercially available from Bayer Corporation
25 (Polymers Division).

The moldable matrix polymer material also comprises a suitable catalyst
composition. The catalyst composition should comprise a catalyst that aids the extent to
which the binder resin and/or the moldable matrix resin cures. Preferably, the catalyst
also aids the speed at which the binder resin and/or the moldable matrix resin cures.
30 Suitable catalysts include, but are not limited to, tert-butylperoxybenzoate (TBPB) and
cobalt naphthanate. In a preferred embodiment, the catalyst is TBPB. In an even more
preferred embodiment the moldable matrix polymer material comprises about 0.50% to
about 2% catalyst composition based on the total weight of the moldable matrix polymer

material and the catalyst composition consists essentially of TBPB. More preferably, the moldable matrix polymer material comprises about 1.50% catalyst composition based on the total weight of the moldable matrix polymer material and the catalyst composition consists essentially of TBPB. Even more preferably, when the moldable matrix resin is a polyurethane formed from the reaction of a polyisocyanate and a polyol added simultaneously to the preform, about 1.5% TBPB based on the total weight of the moldable matrix material is pre-mixed with the polyisocyanate and about 0.25% cobalt naphthanate based on the total weight of the moldable matrix polymer material is pre-mixed with the polyol.

The catalyst composition may be pre-mixed with the moldable matrix resin before the moldable matrix polymer material is added to the string binder or preform to form the molded composite product. Alternatively, the catalyst composition may be added to the moldable matrix resin as the moldable matrix material is combined with the string binder or preform. In a preferred embodiment of the present invention, when the moldable matrix resin is a polyurethane formed from the reaction of a polyisocyanate and a polyol simultaneously introduced around a string binder or preform, then the catalyst composition is preferably premixed with either or both the polyisocyanate and the polyol.

As noted above, the present invention also includes a molded composite product made from the moldable matrix polymer material of the present invention. The molded composite product of the present invention may comprise any suitable string binders.

Accordingly, suitable string binders may integrally comprise a fibrous carrier substrate. Any suitable fibrous carrier substrate may be used. Preferably, the fibrous carrier substrate is selected from the fibrous materials that are commonly known in the art, such as glass, carbon, natural fibers, polymers and other fiberizable materials known in the art, or mixtures thereof. Examples of fibrous carrier substrates that can be used either alone or in combination with glass or carbon fibers include thermoplastics including polyesters such as DACRON®, polyaramids such as KEVLAR® and natural fibers. The fibrous carrier substrate is preferably a fibrous material in the form of continuous strands composed of multiple filaments. The strands may take the form of yarns, or rovings, including two-end and four-end rovings. Preferably, the strands of fibrous carrier substrate comprise reinforcing fibers. Typically, such strands are formed by combining filaments of the reinforcing fibers as they are attenuated from a fiber-forming apparatus such as a bushing or orifice plate, although they may also be made by any method

conventionally known in the art. The filaments may be coated with a suitable sizing composition. For example, a suitable sizing composition may comprise functional agents such as lubricants, coupling agents and film-forming polymers. After being coated with the sizing composition, the filaments may be gathered into strands. These strands may then be formed into yarns or rovings.

Preferably, the diameter of the filaments making up the strands ranges from about 3.5 μm to about 24 μm , preferably from about 9 to about 13 μm . The preferred filament diameters correspond to U.S. filament designations H, G, and K. In the method according to the invention, preferably the strand input has a yield of from about 3,700 yards per pounds (yd/lb) (7459 kilograms per meter (kg/m) to about 7,500 yd/lb (15119kg/m), most preferably about 7,500 yd/lb (15119kg/m), or approximately 66 TEX (g/km measurement reflecting the weight and thickness of the strand).

Any suitable binder resin material may be used in the string binder. Preferably, the binder resin material has a low acid value. As used herein, the term "low acid value" is intended to include a binder resin material that has been modified to have low acidity, as measured by an acid value of less than about 30 mg KOH/g resin. More preferably, the binder resin material is a crystalline resin. Preferably, the acid value of the binder resin material is less than about 10 mg KOH/g resin.

The low acid value that is favored for the binder resin material may be achieved by modifying the end groups of the binder resin molecules to be more compatible with the moldable matrix polymer material that is molded with the string binder to form the molded composite product of the present invention. As a result of this improved compatibility, the binder resin material is able to achieve better integration with the moldable matrix polymer material, and the resulting molded composite product shows reduced blistering upon cure.

The melt viscosity of the binder resin material also plays an important role in the performance of the string binder in the molded composite product of the present invention. For example, where the string binder is comprised of the binder resin material and a fibrous carrier material, if the viscosity of the binder resin material is too low, then upon melting of the binder resin material the molten binder resin tends to wick into the bundles of fibrous carrier material. As a result, insufficient binder resin material is available to cause bonding between the strands of fibrous carrier material, and, consequently, a very soft, weak preform is obtained.

The preferred binder resin compositions that may be used in the practice of this invention include one or more acid-modified thermoplastic or thermosetting resins, such as a low-acid crystalline polyester resin. Preferably, the low-acid crystalline polyester resins are modified resins that are manufactured by controlling the proportions of ingredients and processing conditions during polymerization. The resulting low-acid crystalline polyester resin comprises particular desirable molar proportions of the monomers that are condensed to form the resin. The modified crystalline polyester resin is then transferred to either a fiber drum or release paper and cooled to room temperature, after which the crystalline mass may be broken into small pieces and ground into a coarse powder. Exemplary combinations of crystalline polyester resins that may be formed by polymerization of different monomers include:

<u>Monomers</u>	<u>Molar Ratios</u>
ethylene glycol / fumaric acid	1.0/1.0
1,6-hexanediol / fumaric acid	1.02/1.0
15 1,6-hexanediol / ethylene glycol / fumaric acid	0.82/0.2/1.0
1,6-hexanediol / ethylene glycol / fumaric acid	0.92/0.1/1.0
1,6-hexanediol / 1,4-butanediol / fumaric acid	0.82/0.2/1.0
1,6-hexanediol / 1,4-butanediol / fumaric acid	0.92/0.1/1.0
1,6-hexanediol / 1,4-cyclohexanedimethanol / fumaric acid	0.92/0.1/1.0
20 1,6-hexanediol / 1,4-cyclohexanedimethanol / fumaric acid	0.82/0.2/1.0
1,4-butanediol / fumaric acid	1.03/1.0
1,4-butanediol / ethylene glycol / fumaric acid	0.82/0.2/1.0
1,4-butanediol / ethylene glycol / fumaric acid	0.70/0.3/1.0
1,4-butanediol / ethylene glycol / fumaric acid	0.92/0.1/1.0
25 1,4-butanediol / 1,6-hexanediol / fumaric acid	0.82/0.2/1.0
1,4-butanediol / 1,6-hexanediol / fumaric acid	0.92/0.1/1.0
1,4-cyclohexanedimethanol/ethylene glycol/fumaric acid	0.93/0.1/1.0
1,4-cyclohexanedimethanol/ethylene glycol/fumaric acid	0.83/0.2/1.0
1,4-cyclohexanedimethanol/1,6-hexanediol /fumaric acid	0.83/0.2/1.0
30 1,4-cyclohexanedimethanol/1,6-hexanediol /fumaric acid	0.90/0.1/1.0
1,4-cyclohexanedimethanol/1,4-butanediol /fumaric acid	0.83/0.2/1.0
1,4-cyclohexanedimethanol/1,4-butanediol /fumaric acid	0.90/0.1/1.0

The combination of monomers as described can also be used to affect the melting point of the resulting polymer. For example, the melting points of crystalline polyester resins formed using the combinations described above can have melting points ranging from less than 100°C (212°F) to over 160°C (320°F).

5 In one preferred embodiment, the binder resin is used in conjunction with a catalyst having a high activation temperature, this activation temperature being higher than the melting point of the crystalline binder resin. The role of the catalyst is to effect cure of the binder resin during the manufacture of the preform and/or molded composite product. When activated, the catalyst promotes the formation of a cross-linked product.
10 This catalyst is separate and apart from the catalyst comprising the moldable matrix polymer material of the present invention referred to above.

 Accordingly, the catalyst should be a compound or mixture of compounds that is compatible with the binder resin and which has a temperature of activation that is higher than the processing temperature used to melt the string binder as it is being formed into
15 the preform and/or molded composite product. For example, when the string binder is used to form a preform, the catalyst should have an activation temperature that is higher than the temperature required to melt the binder resin as the string binder is formed into the preform. In this manner, the binder resin polymer may, for example, be used to coat the fibrous carrier substrate, or it may be formed alone as a string binder, without
20 initiating the curing process. Rather, the activation temperature of the catalyst is such that catalytic activity is initiated during the step of curing of the preform. Preferably, the catalyst is activated at the higher temperatures used in preform manufacture. In such applications, the activation temperature of the catalyst is typically in the range of from about 350°F (177°C) to about 400°F (204°C).

25 The catalyst may be combined with the binder resin composition before it is applied to the fibrous carrier material, or alternatively, it may be applied as at least one separate layer of a catalyst composition either as a pre-coating before application of the binder resin composition, or as a post-coating after the binder resin composition is applied. In such embodiments, the catalyst composition may include the catalyst and a
30 diluent, such as water, optionally in combination with other ingredients, such as a carrier material that is compatible with and promotes a uniform solution or dispersion of the catalyst. Thus, in one embodiment of the invention, the catalyst composition may comprise a slurry of catalyst in water. In an alternate embodiment, the catalyst

composition may include the catalyst and a molten carrier material. Where a carrier material is included in the catalyst composition, the carrier material may typically comprise either a thermoplastic or a thermosetting polymer, both of which are commonly known as film formers used in glass fiber fabrication. Preferably, the carrier material
5 comprises a polyurethane, which is desirable because of its good adhesion to glass substrates and its ease of use in glass fiber fabrication processes. The catalyst composition may also comprise conventional additives that are known to improve the adhesion of coating materials to the surfaces of the fibrous carrier substrate. Preferably, the catalyst composition comprises a catalytically effective amount of a suitable catalyst
10 and a thermoplastic carrier, which may, for example, be a polyurethane.

The catalyst composition comprising a carrier material may be prepared, for example, by combining a catalytically effective amount of a suitable catalyst with a molten polyurethane polymer, and the resulting composition applied to a fibrous carrier substrate.

15 Any suitable catalyst may be used. Exemplary families of catalysts that may be used with the string binder include: diacyl peroxides, for example benzoyl peroxide; peroxyesters, for example t-butyl-peroxy-2-ethylhexanoate; dialkyl peroxides such as dicumyl peroxide; hydroperoxides such as cumene hydroperoxide; perketals such as 1,1-di-(t-butyl-peroxy)cyclohexane; and peroxydicarbonates such as di(2-
20 ethylhexyl)peroxydicarbonate. Preferred catalysts include t-butyl perbenzoate and dicumyl peroxide.

The catalyst composition is suitably prepared as either a dilute solution or emulsion in a diluent. Suitable diluents that form a solution or emulsion with the catalyst include water, acetone, methylene chloride, methyl cellosolve, toluene, benzene and the
25 like. Preferably, the catalyst composition is prepared as an emulsion in water because, in such a preparation, the evolution of volatile organic compounds during processing is prevented. When a solvent is used, the proportion of catalyst to solvent may range from about 1 to about 20 parts by weight of catalyst to from about 80 to about 99 parts by weight solvent. (It should be noted that the designation "parts by weight", as it is used
30 throughout this application is intended to designate proportions based on the dry weight of each ingredient). Preferably, about 2-4 parts by weight catalyst may be dissolved in from 96-98 parts by weight solvent. Most preferably, about 3 parts by weight catalyst may be dissolved in about 97 parts by weight solvent.

Alternatively, the catalyst may be emulsified in water, preferably with the use of a suitable surfactant to form a concentrated emulsion which may be stored and diluted as required. In a preferred embodiment of the invention, about 46 parts by weight of molten catalyst are combined with about 6 parts by weight of Pluronic F-77, which is a
5 polyoxyalkylene surfactant commercially available from BASF Corp. The hot mixture is then slowly added to water under very high shear, and the resulting concentrated emulsion is neutralized with ammonia to a final pH of about 9.3. The concentrated emulsion may be stably stored and diluted just before use in the desired proportions for application to the fibrous carrier substrate.

10 The catalyst composition may be applied as a separate coat under, above, or interspersed between coats of the binder resin composition. In one such embodiment of the invention, at least one layer of a solvent-free binder resin composition comprising a thermoformable binder resin material having an acid value of less than about 30 mg KOH/g of resin, and at least one layer of a catalyst composition are applied to a fibrous
15 carrier substrate. For example, the at least one layer of catalyst composition may be applied to the fibrous carrier substrate as a pre-coating before the at least one layer of binder resin composition is applied. As an additional modification, the pre-coating may further comprise a carrier material in combination with the catalyst composition. The pre-coating may be applied in any convenient manner using conventional coating techniques.
20 Such techniques include, for example, spraying, roller or pad coating, wire coating or immersion. Preferably, the pre-coating is applied to the fibrous carrier substrate using a roll applicator, such as a graphite roll, or by immersing the fibrous carrier substrate in a bath containing the catalyst coating solution or dispersion.

It is also possible to apply the catalyst and resin to a strand in a single coating step,
25 if the catalyst and resin are selected such that they can be mixed without prematurely initiating cure of the resin during preform manufacture. Accordingly, in another embodiment, the exemplified crystalline polyester binder resin and the catalyst may be combined and the composition applied to the fibrous substrate at a temperature below the activation temperature of the catalyst. Such a one-step process advantageously allows
30 certain equipment and processing steps to be eliminated, and provides for a more cost-efficient manufacture of the string binder. For example, the binder resin composition may be combined in a static mixer and delivered to a one-step injection die system, wherein the catalyst is added to the binder resin composition immediately before it is coated onto

the surface of the fibrous carrier substrate. When a one-step injection dye is used, a solution or emulsion of the catalyst may not be necessary, and thus this source of waste diluent may be eliminated from the system.

In one example of preparing a binder resin composition for use in a one-step injection dye, a molten binder resin is first prepared by heating powdered binder resin in a hot-melt processor. The catalyst, in dry form, is then added to the processor for combination with the molten binder resin. Optionally, a catalyst composition comprising the catalyst and a solvent could also be used. The selection of the appropriate catalyst and resin system will depend on compatibility of the catalyst and resin, as well as the relative resin melting point and catalyst activation temperature. The processor is linked, by a direct input feed, to a static mixer, thereby allowing the flow of the resin composition containing the catalyst through an outlet disposed in the processor, and through the inlet port of an impregnation or coating-type die. A pump or other conventional flow regulation device controls the feed from the outlet port of the static mixer to the inlet port of the die. The die also comprises an aperture for input of a carrier fiber strand. The direction of movement of the strand input through the die is preferably aligned transverse to the flow of binder resin composition from the static mixer. The strand is then coated by the binder resin composition comprising the catalyst at a temperature below the activation temperature of the catalyst.

Alternatively, the mixture of the binder resin composition including the catalyst may be applied to the strand input of fibrous carrier material using other means, such as a dip-draw immersion bath process.

Before the string binder is used to form the molded composite product of the present invention, the string binder may be co-roved with a reinforcing fiber material to form a multi-end roving product having the desirable characteristics of the novel string binder. This reinforcing fiber material may be selected from glass, polymer, natural fibers, or any combination thereof. Examples of such reinforcing fiber materials include, but are not limited to glass, KEVLAR®, polyaramids, polyesters such as DACRON®, and natural fibers such as linen, jute, hemp, cotton and sisal. Preferably, the reinforcing fiber material is in the form of a continuous roving. To form the co-roved multi-end product, one or more ends of string binder is roved together with one or more ends of a reinforcing fiber material, such as glass, using any conventional winding process. For example, roving ends from 1-3 wound spools of continuously formed string binder of the

present invention may be lined up in a creel simultaneously with roving ends from about 10-20 forming cakes of glass reinforcing fiber strand. Unlike the string binder itself, the reinforcing fiber material used to make the co-roved product is not coated with the low-acid binder resin composition used to form the string binder. This reinforcing fiber material may, however, be sized with an acceptable sizing treatment before being co-roved with the string binder. Application of a sizing treatment typically provides certain desirable effects to the reinforcing fiber material, such as protection from damage by attrition or erosion, and enhances wetout of the fibers in the composite matrix, when molded. Preferably, the sizing treatment is applied to the strands of reinforcing fiber material before they are wound into forming cakes.

The combined ends of the string binder and reinforcing fiber material may then be co-roved or wound together onto a spool, thereby forming a multi-end roving having a proportionate amount of string binder within the roving. The proportion of string binder to the reinforcing fiber material may be varied according to the desired product specifications, the quantities of each being readily determined by one having ordinary skill in the art. Preferably, the proportion of string binder to reinforcing fiber material ranges from about 10% to 15% by weight of string binder to about 85% to 90% by weight of fiber reinforcing material.

Any suitable form of the multi-end roving described above may be used to form the molded composite product, depending on the desired application. For example, the multi-end rovings may be used to form a woven fabric reinforcement, such as a woven roving or a multi-axial stitched reinforcement. Alternatively, the multi-end rovings may also be used, in continuous or chopped form, in various applications requiring an input of reinforcing fiber segments.

In an embodiment requiring input of chopped reinforcing fiber segments, the solidified strand of string binder, or, preferably, the multi-end roving comprising the thermosettable resin-coated string binder, may immediately be chopped into segments instead of being spooled after forming. Preferably, the length of such segments is typically from about .5 inch (1.27 centimeter (cm)) up to about 3 inches (7.62 cm) in length. Most preferably, the chopped segments are from about 1 inch (2.54 cm) to about 3 inches (7.62 cm) in length.

The segments obtained according to the aforementioned procedure are preferably used to make preforms using a spray-up process. An example of such a process is

described in U.S. Patent No. 3,170,197. In a particularly preferred embodiment, segments of a multi-end roving comprising the string binder are blown or spread by conventional means over a shaped preform screen and a sufficient level of heat applied to soften the binder resin enough to permit some fusing of the segments. Preferably, suction is applied to promote compacting of the segments as they fuse. The process of fusing allows the layered material to conform to the shape of the preform screen, and the material is then set into a solid matted structure or preform that can be physically transported if necessary to another location to complete the molding process that forms the final molded composite product. Preferably, the preform is subjected to heat, radiation or other curing means to cure the preform before it is molded.

When a preform is used to prepare the molded composite product of the present invention, the preform typically comprises from about 10% to about 15% by weight of string binder, in combination with from about 85% to about 90% by weight of another reinforcing material. The weight ratio of the amount of fibrous carrier substrate to the amount of binder resin material is preferably about 50:50 in the string binder. To make the preform, the chopped segments of the string binder may be laid up on a consolidation screen, and optionally compressed using suction drawn through the screen to form the material into a desired shape that conforms to the contour of the screen. Preferably, the binder resin in the preform is fully cured before the preform is molded to form the molded composite product of the present invention.

Any suitable molding technique may be used to mold the molded composite product of the present invention from the preform, for example liquid resin molding. Typically, the preform is placed in a mold cavity into which the moldable matrix polymer material of the present invention is injected or otherwise added.

The following examples are representative of the invention.

EXAMPLES

Example 1 – Preparation of Low-Acid Crystalline Resin

A 50-gallon (189 liter) stainless steel reactor configured with a steam-heated packed column and a water-cooled condenser was loaded with 95.57 kilograms (kg) of fumaric acid, 74.21 kg of 1,4-butanediol and 10.22 kg of ethylene glycol. To this mixture was added 16.74 grams of hydroquinone as a polymerization inhibitor. The reactor was heated to about 200°C (392°F) and sparged with nitrogen gas, thereby facilitating a poly-

condensation reaction to form the low-acid crystalline resin, and producing water of condensation as a by-product. Throughout the reaction, the acid value of the crystalline resin was measured using a standard titration against an aqueous potassium hydroxide (KOH) solution, to derive the degree of acidity expressed as the milligrams of KOH
5 needed for neutralization per gram of the resin that was formed.

When the acid value had been reduced to a value from 0 to about 30 mg KOH/g resin, the reaction mass was cooled to a temperature of from about 120°C (248 °F) to about 150°C (302°F), at which time 82.44 grams of t-butylcatechol and 2.70 grams p-benzoquinone was added to the molten mass. (At this point, other compounds may
10 optionally be added, such as from about 1% to about 5% weight of oligo(propylene glycol-alt-maleic anhydride); about 0.25% weight dipropylene glycol and about 1% weight styrene). The resulting low-acid crystalline resin was then transferred to a fiber drum or release paper over a 15-30 minute period, and allowed to cool to room temperature. The solidified crystalline resin was then broken into small pieces and
15 ground into a powder. The final acid value of the crystalline material ranged from about 0 to about 15 mg KOH/g resin. The final viscosity ranged from about 1 poise (0.1 pascal second) to about 25 poise (2.5 pascal second), as measured by cone and plate, with about 12 poise (1.2 pascal second) being preferred.

20 Examples 2-6 — Preparation of String Binders

Example 2

A continuous, single-end strand of G-75 glass yarn (7500 yd/lb (15119 kg/m)) was pre-coated with a catalyst composition comprising a solution of 1.5 parts catalyst in 98.5 parts acetone. The catalyst composition was applied using a graphite roll applicator, after
25 which the pre-coated strand was dried in an oven at a temperature below 177°C (350°F). The dry, pre-coated strand was then passed through a heated bath of binder resin composition comprised of a low-acid crystalline polyester maintained at a temperature of about 133°C (271°F). The low-acid crystalline polyester was prepared according to the scheme described in Example 1 above. The strand impregnated with the binder resin
30 composition was then pulled through a stripper die with an orifice diameter of about 0.012 inch (.031 cm) to remove the excess resin. The resin was then solidified on the strand as it was pulled through an unheated, forced-air cooling chamber at a rate of about 80 feet per minute (fpm) (.41 meter per second (m/s)). At a location about 10 feet (3.048 meter)

from the exit of the die, and before the entrance of the cooling chamber, the strand was exposed to a fine mist water spray to facilitate cooling.

A sample of the cooled strand of string binder was then cut into small pieces of about 3 inches (7.62 cm) in length, and put into an oven at 390°F (199°C) for 4 min. This step served as a quality check to ensure that the low acid crystalline polyester would properly melt and cure during matrix resin impregnation and cure of the composite. At the end of the 4-min. period, the sample was removed from the oven. At that point, the sample was hard and stiff, and a definite color change from white to a clear yellow was observed, indicating a good cure. The LOI (loss on ignition) of the sample was determined to be about 50.3%. This value indicated that approximately 50.3% of the strand weight was organic, non-glass material.

Once the string binder was determined to have an acceptable LOI and to demonstrate good curing ability, it was then chopped into segments and fabricated into preforms.

Example 3

A continuous, single-end strand of G-75 glass yarn (7500 yd/lb (15119 kg/m)) was pre-coated with an water based emulsified catalyst composition comprising 3 parts catalyst and 3 parts PU-403 polyurethane film former (Bayer) or Aquathane 522 (Reichhold), dry solids basis, in 91 parts water. The catalyst composition was applied using a dip bath and stripper die (.012 inch (.031 cm)), after which the pre-coated strand was dried in an oven at a temperature of approximately 107°C (225°F). The dry, pre-coated strand was then passed through a heated bath of binder resin composition comprised of a low-acid crystalline polyester maintained at a temperature of about 133°C (271°F). The low-acid crystalline polyester was prepared according to the scheme described in Example 1 above. The strand impregnated with the binder resin composition was then pulled through a stripper die with an orifice diameter of about 0.0145 inch (.0368 cm) to remove the excess resin. The resin was then solidified on the strand by first passing it through a water mist spray to facilitate cooling. It then traversed an open area interspersed with 2 forced air-drying units (air knives) before being wound onto a package. Overall line speed was 150 fpm (.762 m/s).

A sample of the cooled string binder strand was then cut into small pieces of about 3 inches (7.62 cm) in length, and put into an oven at 390°F (199°C) for 4 min. This step

served as a quality check to ensure that the binder resin would properly melt and cure during matrix resin impregnation and cure of the composite. At the end of the 4-min. period, the sample was removed from the oven. At that point, the sample was hard and stiff, and a definite color change from white to a clear yellow was observed, indicating a good cure. The LOI (loss on ignition) of the sample, which is a measure of the proportion of organic, non-glass material, based on strand weight, was determined to be about 45%. This value indicated that approximately 45% of the strand weight was organic, non-glass material.

10 Example 4

A continuous, single-end strand of G-75 glass yarn (7500 yd/lb (15119 kg/m)) was pre-coated with a water based catalyst composition comprising a solution of 3 parts catalyst, dry solids basis, in 97 parts water. The catalyst composition was applied using a dip bath and stripper die (.012 inch (.031 cm)), after which the pre-coated strand was dried in an oven at a temperature of 107°C (225°F). The dry, pre-coated strand was then passed through a heated bath of binder resin composition comprised of a low-acid crystalline polyester maintained at a temperature of about 133°C (271°F). The low-acid crystalline polyester was prepared according to the scheme described in Example 1 above. The strand impregnated with the binder resin composition was then pulled through a stripper die with an orifice diameter of about 0.0145 inch (.0368 cm) to remove the excess resin. A post-coating was then applied to the strand by passing it through a bath consisting of 6%, on a dry solids basis, of polyurethane emulsion (PU-403, commercially available from Bayer, or Aquathane 522, commercially available from Reichgold), in demineralized water. The post-coated strand was then passed back through the oven at 107°C (225°F) to form the solidified string binder product, then wound into a forming package. Overall line speed throughout the process was 150 fpm (.762 m/s).

A sample of the cooled string binder strand was then cut into small pieces of about 3 inches (7.62 cm) in length, and put into an oven at 390°F (199°C) for 4 min. This step served as a quality check to ensure that the binder resin would properly melt and cure during matrix resin impregnation and cure of the composite. At the end of the 4-min. period, the sample was removed from the oven. At that point, the sample was hard and stiff, and a definite color change from white to a clear yellow was observed, indicating a good cure. The LOI (loss on ignition) of the sample, which is a measure of the proportion

of organic, non-glass material, based on strand weight, was determined to be about 45%. This value indicated that approximately 45% of the strand weight was organic, non-glass material.

5 Example 5

A continuous, single-end strand of G-75 glass yarn (7500 yd/lb (15119 kg/m)) was passed through a heated bath of binder resin composition comprised of a low-acid crystalline polyester maintained at a temperature of about 133°C (271°F). The low-acid crystalline polyester was prepared according to the scheme described in Example 1 above.

10 The strand impregnated with the binder resin composition was then pulled through a stripper die with an orifice diameter of about 0.0145 inch (.0368 cm) to remove the excess resin. A post-coating was then applied to the strand by passing it through a bath containing a water-based emulsified catalyst composition comprising 3 parts catalyst, and 3 parts polyurethane film former (PU-403, or Aquathane 522), in 91 parts water. The

15 catalyst composition was applied using a dip bath and stripper die (.012 inch (.031 cm)), after which the post-coated strand was dried in an oven at a temperature at 107°C (225°F), and wound into a forming package. The overall line speed was 150 fpm (.762 m/s).

A sample of the cooled string binder strand was then cut into small pieces of about 3 inches (7.62 cm) in length, and put into an oven at 390°F (199°C) for 4 min. This step

20 served as a quality check to ensure that the binder resin would properly melt and cure during matrix resin impregnation and cure of the composite. At the end of the 4-min. period, the sample was removed from the oven. At that point, the sample was hard and stiff, and a definite color change from white to a clear yellow was observed, indicating a good cure. The LOI (loss on ignition) of the sample, which is a measure of the proportion

25 of organic, non-glass material, based on strand weight, was determined to be about 45%. This value indicated that approximately 45% of the strand weight was organic, non-glass material.

Example 6

30 A continuous, single-end strand of G-75 glass yarn (7500 yd/lb (15119 kg/m)) was pre-coated with an water based emulsified catalyst composition comprising 3 parts catalyst, dry solids basis, and 3 parts polyurethane film former (PU-403, or Aquathane 522), in 91 parts water. The catalyst composition was applied using a dip bath and stripper

die (.012 inch (.031 cm)), after which the pre-coated strand was dried in an oven at a temperature at 107°C (225°F). The dry, pre-coated strand was then passed through a heated bath of binder resin composition comprised of a low-acid crystalline polyester maintained at a temperature of about 133°C (271°F). The low-acid crystalline polyester was prepared according to the scheme described in Example 1 above. The strand impregnated with the binder resin composition was then pulled through a stripper die with an orifice diameter of about 0.0145 inch (.0368 cm) to remove the excess resin. The strand was then treated with a post coat by passing it through a bath consisting of 6% PU-403 polyurethane emulsion or Aquathane 522 (dry solids basis) in demineralized water. It then was passed back through the oven at 107°C (225°F) before being wound onto a package. Overall line speed was 150 fpm (.762 m/s).

A sample of the cooled string binder strand was then cut into small pieces of about 3 inches (7.62 cm) in length, and put into an oven at 390°F (199°F) for 4 min. This step served as a quality check to ensure that the binder resin would properly melt and cure during matrix resin impregnation and cure of the composite. At the end of the 4-min. period, the sample was removed from the oven. At that point, the sample was hard and stiff, and a definite color change from white to a clear yellow was observed, indicating a good cure. The LOI (loss on ignition) of the sample, which is a measure of the proportion of organic, non-glass material, based on strand weight, was determined to be about 45%. This value indicated that approximately 45% of the strand weight was organic, non-glass material.

Example 7 – Preparation of Molded Composite Product

The effect of adding a catalyst to the moldable matrix polymer material was evaluated to determine its effect on bleeding, i.e., the migration of uncured binder resin to the surface of the molded composite product. Samples of moldable matrix polymer materials were prepared comprising polyisocyanate (Baydur 425 IMR polyisocyanate commercially available from the Bayer Corporation—Polymer Division), polyol (Baydur 425 IMR polyol commercially available from Bayer Corporation—Polymer Division), and certain amounts of certain catalysts. All the samples were prepared in the same way and comprised the same, including amounts of, ingredients, except that the samples were prepared containing varying amounts of various catalysts. Then preforms consisting of five layers of 1.5 ounces (42.5 grams) mat and strands having under-catalyzed string

binder (that is, string binder that does not itself contain enough catalyst to fully cure the binder resin of the string binder) on their top surfaces were placed into a heated (120°F (49°C)) 12 inch x 18 inch (30.48 cm x 45.72 cm) stainless steel tool suitable for reaction injection molding (RIM). The tool included a center gate for injecting the samples of the moldable matrix polymer materials into the tool. Once the preforms were placed into the tool, the tool was closed and the press was set at 300 psi (2068 kilopascals). The samples of the moldable matrix polymer materials were then injected into the tool using a Liquid Controls RTM resin injection unit. The resulting molded composite products were then removed from the tool and allowed to reach room temperature. The molded composite products or plaques were then post cured for about one hour at 300°F (149°F) and then evaluated for resin bleeding.

The results of the evaluation set forth in Example 7 are set forth in the table below:

TABLE

SAMPLE NO.	CATALYST	EFFECT
Control	No catalyst	Heavy bleeding in the molded product
1	0.25% TBPB*	No visual difference from the control.
2	0.50% TBPB*	Slightly less bleeding than the control.
3	0.75% TBPB*	Better than the control, and slightly better than sample no. 2.
4	1.50% TBPB*	About half the bleeding observed compared to the control.
5	1.50% TBPB* 0.25% cobalt naphthanate**	Very little if any bleeding observed.

* Catalyst added to the polyisocyanate.

** Catalyst added to the polyol.

It is believed that Applicants' invention includes many other embodiments which are not herein described, accordingly this disclosure should not be read as being limited to the foregoing examples or preferred embodiments.

WHAT IS CLAIMED IS:

1. A moldable material useful for preparing molded composite products comprising:
 - a) fibers and a thermoset binder for said fibers
 - b) a polymer or polymer precursors; and
 - c) a catalyst capable of acting as a curing aid for said binder.
2. The moldable material of claim 1 further comprising:
 - a) a first layer comprising said reinforcing fibers and said thermoset binder for said fibers
 - b) a second layer comprising:
 - i) said polymer or said polymer precursors, and
 - ii) said catalyst capable of acting as a curing aid for said binder;wherein said first and second layers are optionally adjacent to one another.
3. The moldable material of claim 1 wherein said fibers are selected from a group consisting of glass, carbon, natural fibers, polymers, and mixtures thereof.
4. The moldable material of claim 1, wherein said polymer is selected from the group consisting of vinyl esters, polyesters, polyurethanes, epoxies, phenolic thermoplastics, and precursors thereof.
5. The moldable material claimed in claim 1 further comprising the polymer precursors to polyurethane wherein said precursors are a polyisocyanate and a polyol.
6. The moldable material claimed in claim 1, wherein the catalyst is selected from the group consisting of tert-butylperoxybenzoate and cobalt naphthanate.
7. The moldable material claimed in claim 6, wherein said polymer comprises between about 0.5% and 2% by weight tert-butylperoxybenzoate based upon the total weight of the molded material.
8. The moldable material claimed in claim 7, wherein the moldable material

comprises between about 0.25% and 0.5% by weight cobalt naphthanate based upon the total weight of the moldable material.

9. A product made from the moldable material of claim 1.
10. A molded composite product prepared from:
 - a string binder; and
 - a moldable matrix polymer material, wherein the moldable matrix polymer material comprises a moldable polymer matrix resin and a catalyst composition.
11. The molded composite product claimed in claim 10, wherein the moldable matrix polymer resin is selected from the group consisting of vinyl esters, polyesters, polyurethanes, epoxies and phenolic thermoplastics, and the catalyst composition is selected from the group consisting of tert-butylperoxybenzoate and cobalt napthanate.
12. A method for preparing a molded composite product comprising the steps of:
 - (a) forming a string binder; and
 - (b) introducing a moldable matrix polymer material around the string binder, wherein the moldable matrix polymer material comprises a catalyst composition capable of acting as a curing aid for said string binder;
 - (c) curing the moldable matrix polymer to form the molded composite product.
13. The method claimed in claim 12, wherein the moldable matrix polymer material comprises a moldable matrix polymer resin selected from the group consisting of vinyl esters, polyesters, polyurethanes, epoxies and phenolic thermoplastics, and a catalyst composition selected from the group consisting of tert-butylperoxybenzoate and cobalt napthanate.
14. The method claimed in claim 12, wherein the string binder is prepared by the following steps:
 - (a) forming at least one strand of a fibrous carrier substrate;

- (b) preparing a catalyst composition comprising a catalytically effective amount of a catalyst having a high activation temperature;
 - (c) applying at least one layer of a pre-coating comprising the catalyst composition to the surfaces of the fibrous carrier substrate;
 - (d) applying at least one layer of a solvent-free binder resin composition comprising a thermoformable liquid binder resin material having an acid value of less than about 30 mg KOH/g of resin to the surfaces of the fibrous carrier substrate to form a coated fibrous carrier substrate; and
 - (e) solidifying the coated fibrous carrier substrate to form a string binder.
15. The method claimed in claim 12, wherein the string binder is chopped into segments before the moldable matrix material is introduced.
16. The method claimed in claim 12, wherein the string binder is formed into a preform before the moldable matrix material is introduced.